POTASSIUM FERRATE: A NOVEL CHEMICAL WARFARE AGENT DECONTAMINANT

Russell Greene ***greener@battelle.org*** ***(Battelle Memorial Institute, West Jefferson, OH)***
F. Michael von Fahnestock (Battelle Memorial Institute, West Jefferson, OH)
Bruce Monzyk (Battelle Memorial Institute, Columbus, OH)

ABSTRACT: Chemical warfare agents (CWAs) present a potential threat to military and civilian populations. Current decontamination formulations for CWAs, however, have several shortfalls, including environmental hazards, health hazards, practical use limitations, logistical management difficulties, and/or unsatisfactory CWA destruction efficiencies. Potassium ferrate (K_2FeO_4) addresses all of these issues through its high oxidation potential, stable shelf life, and benign reduced state, namely iron oxide. A series of bench-scale trials on surrogate and actual CWAs demonstrated the potential efficacy of K_2FeO_4 as a viable decontamination agent. Destruction efficiencies using paste and aqueous K_2FeO_4 formulations exceeded 99% for 2,2-dichloroethyl ether, Sarin, Soman, mustard and V-nerve agents. The reaction times were as good as or better than commonly accepted decontaminants, such as bleach and sodium hydroxide.

INTRODUCTION

Chemical warfare agents (CWAs), when used militarily or in terrorist situations, leave a film of active agents on surfaces. These surfaces may include clothing, building structures, vehicles, equipment and many others. There are many conventional decontaminants currently being used for these toxic agents, however many of them have shortfalls. While most are able to effectively destroy the CWAs, many are corrosive to both the skin and the surfaces to which they are applied. For example, chlorine bleach and sodium hydroxide are very effective decontaminants, however, both are corrosive and posses other environmental hazards. In addition, many decontaminants, both actively used and proposed, are unstable (with respect to loss of activity) and/or difficult to prepare, store and transport. Potassium ferrate (K_2FeO_4) has been proven not only to effectively destroy a broad range of CWAs, but also addresses the shortfalls of the currently used CWA decontaminants. Ferrate has many attributes that make it ideal for use as a CWA decontaminant including the following: 1) It is non-toxic on its own. 2) It is an extremely strong oxidant (oxidation potential up to 2.2 volts). 3) It possesses a broad spectrum of uses while it is able to not only decompose organics, but toxic metal ions as well. 4) Its presence can easily be visually monitored as it undergoes a noticeable color change from intense violet to orange as it reacts and is depleted. 5) It is harmless to most surfaces and can be deployed in a number of manners (i.e. paste, powder, spray, and solution).

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The expected oxidation and hydrolysis reaction (unbalanced) involved in general terms is as follows (written for the CWA Sarin reaction with ferrate),

$FeO_4^{=}$ + $(CH_3)_2CHO\text{-}P(F)(=O)(CH_3)$ → $\underline{FePO_4}$ + $\underline{FeF_3}$ + HCO_3^- + $\underline{FeOOH}$
Ferrate Sarin nontoxic mineralized products

Where the hydrated $FePO_4$, Fe_3, and FeOOH products are common, stable, nontoxic materials. Also, the mild pH 8 buffer HCO_3^-, is a nontoxic, water-soluble ion that is the major component of baking soda. The specific reaction stoichiometry will depend on the type of CWA involved, other oxidizable materials present, etc. In use, excess ferrate would be added to ensure complete CWA defeat (excess ferrate would be monitored easily by the purple color of the $FeO_4^{=}$). The excess $FeO_4^{=}$ readily and completely decomposes to rust within seconds to minutes depending on pH. Ferrate can be decomposed within seconds by washing/spraying with any number of mild reagents, including dilute vinegar solution, carbonated water or soap and water.

Preliminary proof-of-principal testing was conducted at Battelle's Hazardous Materials Research Center (HMRC) and Process Engineering Laboratories to determine the efficacy of potassium ferrate as a CWA decontaminant. The purpose of this paper is to outline the testing that was conducted and the resulting data that was obtained.

LABORATORY TECHNICAL APPROACH

The overall objective of the laboratory studies was to generate data proving the decontamination concept of potassium ferrate. The studies summarized in this paper are proof of principal tests; by no means do they illustrate the full extent to which ferrate could be used as a CWA decontaminant. The laboratory testing included three different areas of testing, all directly related.

Large Volume/High Water Content Tests. The first phase of testing included high water content (relative to other phases of testing), large volume kinetics studies. Purified potassium ferrate was prepared in powder form at the Process Engineering laboratories at Battelle-Columbus, OH. All CWA testing was conducted at the HMRC chemical surety laboratories at Battelle-West Jefferson, OH. The CWAs used in this phase of testing were Soman (GD), VX and mustard (HD). A 25 mL aqueous solution of potassium ferrate and water was prepared in round bottom flasks immediately before testing. 500 mg of a specific CWA was added to the solution and stirred for 1 hour. Aliquot samples were taken at predetermined times, a liquid chloroform extraction performed and the samples analyzed for residual CWA using a Gas Chromatogram (GC) equipped with either a Flame Photometric Detector (FPD) or Flame Ionization Detector (FID).

Large Volume/High Water Content Tests with Phase Transfer Catalyst. After examining the data from the first phase of testing (summarized later in this paper), a determination was made to introduce a Phase Transfer Catalyst (PTC) into the ferrate decontamination formulation. The need for the PTC arose due to high water insolubility of some CWAs, specifically HD and VX. It is hypothesized that the destruction of HD

and VX was hindered by mass transfer in the presence of large amounts of water. The insoluble characteristics of these agents, causes a high level of partitioning and in many cases, droplets of agent are visibly present in the solutions. A unique product was formed by combining a quat and ferrate. Specifically, Aliquat 336 [$(CH_3(CH_2)_8)N^+X^-$] was utilized were the two quaternary ammonium ions are separate molecules. Other PTCs, along with emulsifiers and wetting agents were screened in bench-scale tests involving ferrate and CWA surrogate 2,2-dichloroethyl ether (HD surrogate). The results of these tests are not discussed in this paper, other than to state that Aliquat 336 was selected for use in the subsequent trials.

Once the surrogate screening process was completed, a test was conducted using HD. The CWA was again added directly to a 25 mL decontamination solution, this time containing ferrate and the PTC. Samples were taken at the completion of a two-hour test time, and samples taken for analysis via GC-FPD/FID.

Small Flask Reactions. A third series of tests were performed with the CWAs VX and HD. The objective of these experiments was to further examine the effectiveness of the ferrate/PTC formulation. The agents VX and HD were specifically examined due to their hydrophobic characteristics. The determination was made, that these two agents represented the worst-case scenario. The small flask reactions were divided into two types: “wet” and “dry.” The “wet” experiments consisted of a 5 mL decontamination solution of different combinations of ferrate, PTC and the pH buffer KH_2PO_4. An approximate decontaminant:CWA molar ratio of 14:1 was used. The specific test matrices are outlined in following sections of this paper. The tests were conducted in 20 mL scintillation vials and stirred with a magnetic stir bar for 2 hours. The “dry” experiments were the same as the “wet” tests, with the exception of the water. There was no water added to the decontamination formulation, resulting in a paste-like decontaminating agent. In both the “wet” and “dry” tests, the entire matrix was extracted in chloroform at the completion of the test run and an aliquot of the extraction analyzed with a GC for residual CWAs.

RESULTS AND DISCUSSION

As stated earlier, the testing discussed in this paper was conducted in three phases. The summary and discussion of the results will be separated by the three test phases.

Large Volume/High Water Content Results. Promising destruction results for the nerve agent GD were accomplished in this first phase of testing. Figure 1 illustrates the concentration of GD (μg/mL) in the solution over time. There was a ferrate:GD molar ratio of approximately 7.1 in these tests. All tests lasted 2 hours with specific sampling times throughout the length of the test, which were run in triplicate. A “positive” control sample was included in the test, which consisted of a 25 mL solution of solvent that the GD was spiked into. The purpose of the “positive” control was to validate the agent application, sampling and extraction process. All “positive” controls remained within an acceptable range of the theoretical concentrations. As shown in Figure 1, greater than 99% of the GD was destroyed within 15 minutes of reaction time. The results however, were less promising for the nerve agent VX. As shown in Figure 2, there was an initial spike in

Figure 1

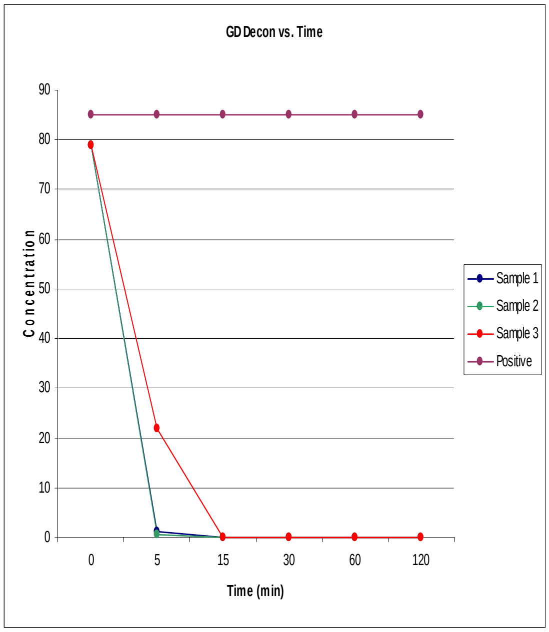
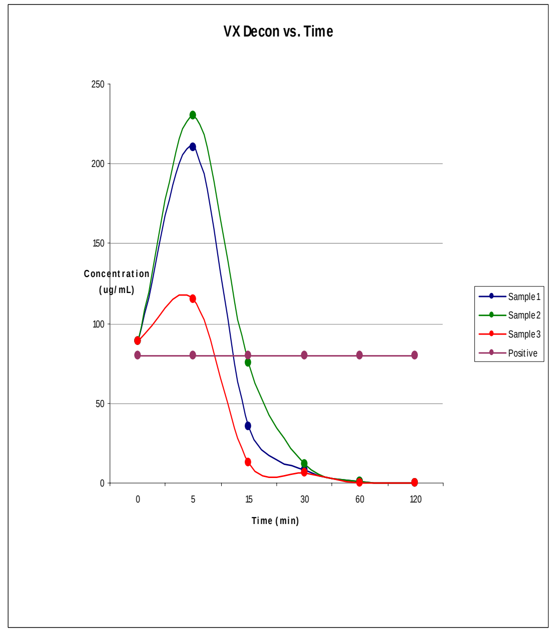


Figure 2



concentration at the first sampling time. In fact, the concentration was higher than the theoretical concentration as well as the "positive" control. It was hypothesized that the erratic concentrations were a result of a non-homogeneous solution. Because of the insolubility of VX in water, pockets of agent were forming in the solution. It was this fact, as well as similar results with HD, that led the test team to investigate the use of PTCs.

Large Volume/High Water Content with Phase Transfer Catalyst Results. A small amount of testing was conducted utilizing the ferrate/PTC formulation in the larger volume/high water content reaction tests. CWAs GB and HD were tested in this phase, with the GB exhibiting similar destruction rates as the GD from the first phase of testing. In fact greater than 99% of the GB was destroyed within 5 minutes of reaction time. This is not surprising, considering the high water solubility of GB. The GB test was identical to the previous tests described above, but included the PTC Aliquat 336.

A similar test was conducted with HD, however, rather than sampling at specific times throughout the length of the test, samples were only taken at the conclusion of the test. The tests were run in 250 mL round-bottom flasks with overhead stirring. The tests were run for 2 hours and triplicate samples taken from each flask at the completion of the test run. Table 1 shows the test matrix and the results of the test. As illustrated in the table, all samples exhibited greater than 90% destruction of the HD. In retrospect, sample 2 two should have been without the PTC. Because sample number 2 exhibited greater than 90% destruction of HD, the results are not completely conclusive that the ferrate was responsible for the destruction of the HD. In fact, it could be that with the PTC present in sample 2, it allowed the HD to be hydrolyzed in the water. The third phase of testing addresses this issue through control samples which narrow down the effect of the individual components.

Table 1.

RUN #	AMOUNT OF AGENT (mg)	PTC AMOUNT (g) (Aliquat 336)	PURIFIED K2FeO4 AMOUNT	DI WATER/ BLEACH AMOUNT	.pH Buffer (g)	Results (µg/mL)
1.A	637 mg	1.0 g	7.0 g	25 mL DI Water	13 g	<0.5
1.B	"	"	"	"	"	<0.5
1.C	"	"	"	"	"	<0.5
2.A	637 mg	1.0 g	0	25 mL DI Water	13 g	16.75
2.B	"	"	"	"	"	5.71
2.C	"	"	"	"	"	24.1
3.A	637 mg	1.0 g	0	25 mL Bleach	13 g	<0.5
3.B	"	"	"	"	"	<0.5
3.C	"	"	"	"	"	<0.5

Small Flask Reactions Results. From the first two phases of testing, it was determined that HD and VX presented the greatest challenge for destruction. To address this challenge, additional testing was conducted utilizing the ferrate/PTC formulation. However, in this phase, the reactions took place on a smaller scale with lower amounts of both decontaminant and CWA. Table 2 and Table 3 illustrate the test matrices for two of the test runs, as well as the results.

Table 2.

Sample ID	AMOUNT OF VX (mg)	PTC AMOUNT (mg) (Purified Aliquat 336)	PURIFIED K_2FeO4 AMOUNT (mg)	DI WATER	.pH Buffer KH_2PO_4 (mg)	Total Remaining VX (mg)	% Destruction
49788-50-1	10.1 mg	40 mg	260 mg	0	140 mg	**1.65**	**83.7**
49788-50-2	10.1 mg	40 mg	260 mg	0	140 mg	**0.776**	**92.3**
49788-50-3	10.1 mg	40 mg	260 mg	0	140 mg	**0.657**	**93.5**
49788-50-4	10.1 mg	0	0	0	140 mg	**7.87**	**22.1**
49788-50-5	10.1 mg	0	260 mg	0	140 mg	**3.71**	**63.3**
49788-50-6	10.1 mg	40 mg	260 mg	5 mL	140 mg	**BDL**	**>99**
49788-50-7	10.1 mg	40 mg	260 mg	5 mL	140 mg	**BDL**	**>99**
49788-50-8	10.1 mg	40 mg	260 mg	5 mL	140 mg	**BDL**	**>99**
49788-50-9	10.1 mg	0	0	5 mL	140 mg	**3.69**	**63.5**
49788-50-10	10.1 mg	0	260 mg	5 mL	140 mg	**0.005**	**>99**

Table 3.

RUN #	AMOUNT OF HD (mg)	PTC AMOUNT (mg) (Purified Aliquat 336)	PURIFIED K_2FeO4 AMOUNT (mg)	DI WATER AMOUNT	.pH Buffer KH_2PO_4 (mg)	Results Total Mass Remaining (mg)	% Destruction
3.A	12.5 mg	40 mg	260 mg	0	140 mg	**1.22 mg**	90%
3.B	12.5 mg	40 mg	260 mg	0	140 mg	**1.60 mg**	87%
3.C	12.5 mg	40 mg	260 mg	0	140 mg	**2.69 mg**	79%
3.D	12.5 mg	40 mg	0	0	140 mg	**11.15 mg**	11%
3.E	12.5 mg	0	260 mg	0	140 mg	**9.96 mg**	20%
4.A	12.5 mg	40 mg	260 mg	5 mL	140 mg	**1.10 mg**	91%
4.B	12.5 mg	40 mg	260 mg	5 mL	140 mg	**1.50 mg**	88%
4.C	12.5 mg	40 mg	260 mg	5 mL	140 mg	**1.38 mg**	89%
4.D	12.5 mg	0	0	5 mL	140 mg	**1.68 mg**	87%
4.E	12.5 mg	0	260 mg	5 mL	140 mg	**< 0.5 mg**	+ 99%

As shown in the above tables, results for both HD and VX exhibit similar properties. In each of the tables, note that the first five samples are the “dry” tests (no water added) and the second five are the “wet” tests (5 mL of water added). It is apparent from the results of the “dry” samples, that removal of the phase transfer catalyst from the decontamination formulation significantly inhibits the destruction of the CWA. This does not seem to be the case in the “wet” samples. More testing will need to be conducted to effectively determine the mechanisms effecting the reactions. However, the percent destruction of the CWA by the decontamination solution remains promising. It should be noted that visual observations made during laboratory tests, indicated a concern that during mixing, some of the CWA may have “splattered” onto the upper walls of the reaction flask, thus not allowing it to come in contact with the decontaminant. With the entire contents of the flask being extracted at the completion of the test, all CWA would have been detected, whether it had been it contact with the decontaminant or not.

FURTHER TESTING

While results from the initial proof-of-principal testing are promising, it is certainly necessary to conduct further testing. Further testing would determine the full extent of the ability of potassium ferrate to act as a viable CWA decontaminating agent. In addition, it would allow refinement of ideal use conditions, examination of deployment methods, determination of regulatory compliance ability and increased efficacy of ferrate in the presence of larger volumes of water. Specific testing may include: 1) Defining decontamination use procedures, refine formulation. 2) Identify and evaluate ferrate

formulated and physical product forms. 3) Verify complete detoxification by assaying for problem CWA intermediates, etc. 4) Perform contaminated-surface decontamination testing (coupon testing). 5) Perform side by side comparison studies with currently accepted decontaminants.

CONCLUSIONS

The chemical properties of potassium ferrate represent a very attractive candidate for a CWA decontaminant. Ferrate is able to address the shortfalls of the currently used and proposed decontaminants, while efficiently destroying the toxic agents. The testing discussed in this paper by no means proves the extent to which ferrate can be used in this role, however it certainly proves the basic chemical principals are accurate and that further testing regarding this topic is worthwhile. The unique formulation of the potassium ferrate combined with a PTC could very well prove to be a significant breakthrough. It is also important to note that preliminary data generated from other studies indicate that potassium ferrate is a viable biological warfare agent decontaminant as well. Other studies conducted at Battelle yield promising data for the destruction of Highly Energetic Materials, namely munitions. This, combined with the data produced in the study detailed in this paper, are evidence that potassium ferrate has the potential of fulfilling the role of a universal decontaminant. Again, not only are the destruction efficiencies attractive, but the benign nature of the compound and its reaction products as well. The applications could be significant in both a civilian and military sense.